



# Ground and excited state properties of alizarin and its isomers



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## ABSTRACT

Four different alizarin dyes are studied with optical, electrochemical and quantum-chemical techniques. Despite structural similarities they show marked differences regarding both ground and excited state properties. All these dyes are characterized with strong HOMO–LUMO transitions of internal charge transfer character. These transitions, however, show different reorganization energies due to involvement of intramolecular proton transfer processes. Differences in charge redistribution upon excitation may lead to different photochemical reactivity of these species and also to different behavior in dye-sensitized solar cells and other devices.

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## 1. Introduction

Rapid development of photocatalysis [1], photovoltaics [2], and infochemistry [3] relies on novel materials with precisely tailored properties. Furthermore, the synthesis of these materials should be cheap and environmentally-friendly. A large variety of organic chromophores, displaying desired properties can be used as semiconductor surface modifiers or exploited directly as functional materials in numerous applications. In particular, dihydroxyanthraquinones (DHAQs) constitute an interesting family of compounds. They are anthraquinone dyes bearing –OH and C=O moieties which may be used to anchor these dyes to semiconductor surfaces. Scheme 1 presents the most relevant structural isomers of DHAQs. These dyes are easily distinguishable by their color which varies from greenish yellow for anthrarufin, yellowish orange for alizarin, intense orange for chrysazin to dark red for quinizarin.

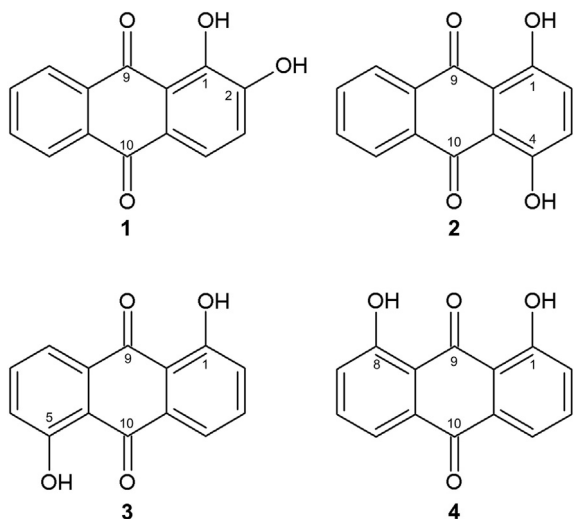
Physical form of these dyes in the pure form also varies. Alizarin (C.I. 58000), quinizarin and anthrarufin are usually fine powders, whereas chrysazin occurs as well developed crystals. The variety of colors of the above species is a result of different electronic transitions and different type of electron delocalization manifolds within molecules. Despite structural similarities, dihydroxyanthraquinones present surprisingly different redox and spectral characteristics and thus find different applications.

The leading example of anthraquinone derivative used as a dye is alizarin, known as Turkish red or Mordant Red 11. The discovery of a synthetic method of alizarin fabrication in the second half of the 19th century revolutionized the textile industry. The British Army red coats serve as a good example of large scale production of colored fabrics. The affinity of alizarin towards the p-block (aluminum, tin, lead) and d-block (zinc, copper, cadmium, cobalt, nickel, iron, chromium, zircon, scandium) cations is well documented. Formation of strongly colored complexes (usually of low solubility in water) is commonly used for trace metal extraction and quantification [4–6]. Its ability of binding calcium makes alizarin useful in biochemical studies involving bone growth and osteoporosis, gene expression and tissue engineering [7–9]. It is also used in geology as a marker of calcium containing minerals [10] or in ore-mining industry as an organic foam depressant in the flotation

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**Scheme 1.** Molecular structure of alizarin (1), quinizarin (2), anthrarufin (3) and chrysazin (4).

process [11]. It is also suitable in fluorimetric detection of boron compounds and fluoride anions [6,12–14]. 1,4-dihydroxyanthraquinone has received some attention as an anticancer drug [15]. It is used also as a fungicide and a pesticide. Furthermore, it finds niche applications as an additive in lubricants. Quinizarin forms fluorescent complexes with lithium, boron and aluminum which makes it useful for spectrofluorimetric detecting of these elements [16,17]. Anthrarufin was found to be active against Gram-positive bacteria, as well as it reduces damaging effects of dioxin [18]. Chrysazin (also known as danthron) has been widely used as a laxative till the eighties, when American manufacturers withdrew this compound from drug production because of carcinogenic risk for human. Chrysazin is also widely used in some metal ion determinations, e.g. lithium, magnesium, calcium, copper, lead, cadmium, zinc, nickel, manganese, iron, cobalt, palladium and platinum [19]. Photochemical reduction of some dihydroxyanthraquinones leads to the generation of semiquinone radical anions and a number of reactive oxygen species including singlet oxygen  $O_2(^1\Delta_g)$  [20–23]. The anthraquinone derivatives also are commonly used in electrocatalytic processes, for example for reduction of molecular oxygen [24–26]. Alizarin and quinizarin naturally occur in the roots of the madder plant (*Rubia tinctorum*), anthrarufin is found in some species of fungi (*Aspergillus glaucus*, *Trichoderma sp.*) and bacteria (*Xenorhabdus sp.*), chrysazin can be extracted from dried leaves and stems of *Xyris semifuscata*, a plant harvested in Madagascar.

Even though those compounds have been known for centuries, mainly because of their coloring properties, their chemistry has recently received a lot of attention in relation to their use as  $TiO_2$  surface modifiers [24,27–34]. Alizarin– $TiO_2$  couple becomes a model system for examining dynamics of the electron injection from the molecule to the semiconductor in the weak electronic coupling regime [29–33,35–38]. Alizarin is a good photosensitizer, and arouses great interest as a modifier in dye-sensitized solar cells. Recently some DHAQ dyes were involved in the synthesis of  $TiO_2$ -based materials for optoelectronic systems [27,28]. This class of photoactive materials reveals unusual photocurrent–voltage curves. Particularly, the  $TiO_2$  electrodes modified with alizarin and alizarin complexone ligands show both anodic and cathodic photocurrents depending on the applied external potential. Anodic photocurrents are observed when an excited electron is transferred from the conduction band of the semiconductor towards the

conducting support with the concomitant oxidation of the redox mediator present in the electrolyte. In contrary, cathodic photocurrents are generated when an electron from the conduction band (or from a sensitizer-based surface state) is transferred to the redox mediator present in the electrolyte. This phenomenon is called photoelectrochemical photocurrent switching effect (PEPS) [39,40]. Materials revealing PEPS have great potential in optoelectronics as they can be used for construction of optical switches, logic gates and other information processing devices [39–50]. The knowledge about ground and excited states of the aforementioned molecules is also relevant in photovoltaics and photocatalysis, where dyes are implemented in sophisticated structures often containing semiconductor or metal nanostructures. Information on adsorption properties of molecules and its ability for self-organization as well charge donating character is indispensable in designing efficient hybrid systems.

Previous works describe ionic forms [51], tautomerism [36,52] or photocatalytic properties [22] of dihydroxyanthraquinones. Recent reports also emphasize the role of geometry of the photosensitizer molecule on the mechanism and efficiency of photoinduced processes at the  $TiO_2$  surface [24,27,53]. However, there are no comprehensive studies on spectroscopy and electrochemistry of the dihydroxyanthraquinone dyes which take into account the positional isomerism. The special emphasis is placed on possible forms of the dyes in the solid as well as in liquid phases (solutions). The present study involves four dihydroxyanthraquinone dyes (Scheme 1): alizarin (1), quinizarin (2), anthrarufin (3) and chrysazin (4), and describes their spectroscopic and electrochemical properties. Experimental data are supported with DFT and TD-DFT calculations of molecular geometry, electronic structure and excited state properties. All DHAQs, due to the presence of an electron donor (phenolic) and electron acceptor (quinone) moieties, can be considered as electrochemically amphoteric species. This type of molecules is especially interesting from the point of view of molecular electronics [54].

## 2. Experimental

### 2.1. Materials and methods

All the organic dyes were of the highest purity available and used as purchased. Dye 1 was delivered by *Acros Organics* whereas 2, 3 and 4 were supplied by *Alfa Aesar*. HPLC grade solvents of 99.9% purity were purchased from *POCH* (acetonitrile, ACN) and *Sigma–Aldrich* (dimethylformamide, DMF). The absorption spectra of dyes dissolved in either ACN or DMF were recorded on Agilent 8453 (*Agilent*, USA) spectrophotometer in quartz cell of 1 cm optical path length. Luminescence spectra were recorded on Fluoromax-4P (*Horiba Jobin Yvon*, France) spectrofluorimeter, in quartz cell of 1 cm optical path length. Diffuse reflectance spectra were recorded on Lambda 950 spectrophotometer (*Perkin Elmer*, USA) equipped with 150 mm integration sphere. For reflectance spectroscopy the samples were dispersed in spectrally pure  $BaSO_4$ . To obtain homogeneous sample the dyes in a first step were dissolved in ACN or DMF before grinding with  $BaSO_4$ . The same  $BaSO_4$  was used as a white standard. Recorded reflectance values were converted to the Kubelka–Munk function ( $\alpha'_{KM}$ ) according to Eq. (1):

$$\alpha'_{KM}(h\nu) = \frac{[1 - R(h\nu)]^2}{2R(h\nu)}, \quad (1)$$

where  $R$  stands for reflectance. The resulting spectra were multiplied by the energy of light quanta ( $h\nu$ ) in order to preserve the Gaussian envelope of electronic transitions [55]:

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